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Determination of Total Particulate
Matter (Dry) and Nicotine in Ciga-
rette Smoke

The following statement of methods and procedures for the determination of water-free Total Particulate Matter (TPM) and total alkaloids as nicotine (hereinafter referred to as nicotine) represents the consensus of major laboratories of the industry with only minor exceptions as noted. It should be emphasized that industry laboratories have long and extensive experience in cigarette testing. The comments which follow are based on this experience and reflect the need to observe certain precautions if reliable test results are to be obtained.

In preparing these recommendations the aim has been to obtain results which are reliable to plus or minus 5% of the reported value at the 95% confidence level. This statement would be statistically interpreted to mean that the true value of total particulate matter for a given sample reported as 20 mg per cigarette would be in the range of 19 to 21 and that in so concluding the investigator would be right 95 times out of a hundred. It can also be shown statistically from a consideration of the collaborative study by C. L. Ong, J.A.C.A.C., 47, 356 (1955) that to achieve this precision for a given sample approximately 400 cigarettes must be smoked. This point will be amplified in a later section.

Sampling

If the objective of a cigarette testing program is to demonstrate differences between brands, a sampling procedure must be established so that the data obtained fairly reflect the characteristics of the product as a whole. Note that individual cigarettes within a given brand, or groups of cigarettes as represented by a package or carton, may vary in terms of cigarette weight, uniformity of blend, age, moisture content, filter dimensions, burning rate, etc. All of these may affect the particulate matter and nicotine delivery of the cigarette to a greater or lesser degree. Reliable characterization of a brand as the consumer receives it, therefore, requires selection of the sub-sample to be smoked from a larger sample population made up of cigarettes obtained from many locations.

A recommended procedure would be to pick up 100 packages of cigarettes for each brand to be tested from fifty locations throughout the country. This pick-up may be accomplished through an outside contractor such as Western Union,

Sub-samples

The sub-samples for smoking should be selected, as described below, from the one-hundred package sample which has been previously collected from fifty retail locations geographically distributed throughout the United States.

The packages are carefully opened and three cigarettes are randomly selected from each package. These cigarettes are pooled and now represent a three hundred cigarette pooled sub-sample which after conditioning will supply the 200 cigarettes needed for smoking. (Comments on conditioning procedure will be made later.)

As cigarettes are required for smoking, 5 cigarettes are randomly selected from the conditioned, pooled sub-sample and are combined to provide a 5 cigarette "port" sample. This procedure is repeated each time a 5 cigarette "port" sample is required until the necessary number of "port" samples has been obtained. It is recommended that 40 "port" samples be smoked for each cigarette brand analyzed.

The rationale for choosing forty as the number of "ports" to be smoked is derived from the estimate of precision given in the Ogg paper. This paper reports upon the application of a smoking method to two rather uniform lots of cigarettes specially made for the study. Using this rather ideal situation, it is possible to estimate the number of cigarettes which it is necessary to smoke in order to report TPM values to a given degree of precision with 95% confidence.

From the student's "t" test;

$$n = \frac{t^2 \sigma^2}{E^2}$$

where n = the number of cigarettes smoked

t = the student "t" value which is dependent upon the level of confidence desired. For 95% confidence it may be taken as 2.

σ = the standard deviation

E = the maximum error which one wishes to tolerate with a given level of confidence

The value for the standard deviation is derived from Ogg (Table 3, $\sigma = 3.19$) for the mean standard deviation between laboratories. Since this value is based on one port (5 cigarettes), it is necessary to multiply by $\sqrt{5}$ to convert this to a per cigarette basis.

Thus:

$$\sigma = 3.19 \times \sqrt{5} = 7.1$$

The choice of the standard deviation between laboratories was chosen since even if all determinations are to be made in a single laboratory it will be necessary to report values to a degree of precision which would be expected if they were verified by other qualified, independent laboratories.

Thus for reporting to the nearest milligram:

$$\sigma = 7.1$$

$$E = 1$$

$$\longrightarrow 0.5$$

$$t = 2$$

$$n = \frac{(2)^2 (7.1)^2}{(1)^2} = \underline{201.6}$$

or approximately 200 cigarettes.

It is interesting to note that in order to establish results to tenths of milligrams with the same confidence in the same idealized situation the number of cigarettes needed to be smoked gets very large indeed.

$$n = \frac{(2)^2 (7.1)^2}{(0.1)^2} \approx 20,000$$

Despite the fact that the above calculations do not take into account many additional variations which must be considered in trying to estimate a value which is representative of a brand as purchased in the market place, it is suggested that they be used as a first approximation of the number of cigarettes to be smoked. It is believed that proper use of a monitor sample (described later) will reduce procedural variations, and in any event appropriate statistical evaluation of continuing samples will indicate the extent to which the sampling is adequate.

Cigarettes to be smoked should not contain soft spots nor be loosely packed or frayed at either end. In the final selection of cigarettes for smoking, damaged or defective cigarettes should be discarded and replaced

with additional cigarettes drawn from the conditioned, pooled sub-sample.

If the "port" sample is selected and/or prepared for smoking in a room which is not maintained at the same temperature and relative humidity at which they were conditioned, the cigarettes should be reconditioned before smoking.

Cigarette sample selection and cigarette smoking should be carried out in a laboratory room maintained at $75 \pm 2^\circ \text{F}$ and $60 \pm 2\%$ relative humidity.

Sample Conditioning

In the opinion of a large majority of the tobacco industry laboratories cigarettes should be conditioned prior to smoking. However, one major laboratory dissents from this opinion. This laboratory believes that when smoke analyses are made for the purpose of comparing brands sampled from the market, the cigarettes should, as far as possible, be smoked at the same moisture content which they had when purchased. On the other hand those laboratories recommending conditioning feel that it is necessary because otherwise the moisture content of the cigarettes smoked will be a function of both the age of the cigarette and the ambient conditions at which the cigarettes are stored not only in the wholesale and retail outlets but also while being held prior to analysis. This variability in moisture content will, in turn, affect the burning rate and therefore the

nicotine and TPM delivery of the cigarettes.

If cigarettes are to be conditioned, they should be placed loosely upon wire mesh shelves in a space in which the temperature and relative humidity are adequately controlled. It is recommended that cigarettes be conditioned at $75 \pm 2^\circ \text{F}$ and $60 \pm 2\%$ relative humidity for a period of time sufficiently long to allow the cigarettes to come to moisture equilibrium with the atmosphere of the conditioning chamber. The exact time required will depend to a large extent upon the rate of flow of conditioned air around the cigarettes. Once the conditioning facilities are operating, simple experimentation can establish the time required for cigarettes to attain a constant weight. This time should be adopted as a standard procedure provided that conditions such as air flow, cigarette loading, chamber geometry, etc. are not changed.

Industry experience indicates that conditioning cigarettes in desiccators over constant humidity solutions is cumbersome, requires a very large number of desiccators and takes an inordinately long time for the cigarette to reach equilibrium.

Monitor Sample

It is common in analytical work to include check samples in order to be certain that the results

obtained on unknowns are valid. This concept is especially important with smoke analytical procedures because experience, in various tobacco industry laboratories, has shown that there are unexplainable day-to-day variations in our analytical results obtained on a single sample. To obtain valid smoke analytical results on diverse samples over a period of time, it is essential to make daily checks on a carefully prepared monitor cigarette. The daily results for the monitor may be related to the average for this sample over a period of time and the results obtained on other samples may be corrected for the day-to-day variation in analytical results.

In the manufacture of a satisfactory monitor sample, extra care should be used in blending the tobaccos, in the selection of uniform cigarette paper and filters and in fabrication.

The monitor cigarettes should be conditioned in accordance with the procedures described above. The number of monitor samples which should be smoked daily will depend upon the uniformity of the particular sample, the degree of control over smoking variables and the accuracy desired. This number can only be determined by experience and statistical considerations.

There are many details associated with the production and use of a monitor sample which are beyond the scope of this discussion. Additional information and assistance in the production of a satisfactory

monitor sample will be provided if desired.

Smoking Machine Characteristics

Each laboratory of the industry has done considerable work on development of analytical procedures for determination of nicotine and TPM in mainstream smoke. In spite of this, as noted by Ogg, further work is believed to be necessary to obtain a totally satisfactory method.

Nonetheless for strictly analytical purposes the puff characteristics in the Ogg method, although arbitrarily chosen, are exactly defined. Several different smoking devices are being used in the industry to achieve these puff characteristics.

However, the automatic smoking machine which is selected should be capable of achieving the following puff characteristics with all types of cigarette:

Puff Volume. - 35 ± 0.5 ml measured as volume of smoke that will be drawn from the butt end of the cigarette under actual machine smoking conditions. Puff volume should be checked before and after each analytical smoking run with smoke collection trap in system.

Puff volume should be measured using a soap bubble manometer.

Puff Duration. - 2 ± 0.2 sec. measured at the cigarette under actual machine smoking conditions by a soap bubble manometer and a suitable timing device.

Puff Frequency.- 1 puff per 60 \pm 1 sec.

Volume Between Filter Holder and Machine.-

Volume between the filter holder and the puffing device should be kept to an absolute minimum.

The area in which the cigarettes are smoked should be as free as possible from all drafts.

Cambridge Filter Assembly*

(a) Filter holder.- A Lucite (or aluminum) filter holder consisting of threaded inner and outer parts and Teflon gasket.

(b) Filter disc.- Cut discs 1.74" (44 mm) in diameter from CML13A fiber glass sheet made by the Cambridge Filter Corp., 738 Erie Blvd., East Syracuse 3, N.Y., or equivalent filter material. Filters must collect at least 99.9% of all particles 0.3 μ in diameter and over at a flow rate of 28 linear ft. per min., have a maximum pressure drop not exceeding 93 mm water at 28 ft. per min., and contain not more than 5% acrylic-type binder.

It is recommended that in ordering filter material specifications as given above should be clearly stated.

(c) Lucite guide.- A Lucite guide is used to assist in placing the rubber membrane on the filter

*For a detailed description of smoking apparatus see Wartman, W.B., Cogbill, E. G., and Harlow, E. S., Anal. Chem., 31, 1705 (1959).

holder. (The holder, guide, and filter medium, CML13A, both in sheets and as 1.74" diameter discs, are obtainable from Phipps and Bird, Inc., Richmond, Va.)

(d) Rubber membrane.-- Cut a square piece of medium latex dental dam, approximately 3.5 x 3.5 cm. Place between two pieces of rubber tile, or other suitable material, and punch a hole 4-6 mm in diameter in the center of the sheet with a cork borer of appropriate size; the size of the hole depends on the circumference of the cigarettes. Latex rubber sleeves, 8 mm in diameter and 20 mm long, may also be used.

(e) Rubber "O" ring.-- An "O" ring, 3/8" i.d., may be made by slicing off a thin section of 3/8" i.d. rubber tubing or may be purchased from Linear, Inc., State Rd. & Levick St., Philadelphia, Pa.

Smoking Procedure

Using the Lucite guide, place a rubber membrane on the filter holder by inserting the offset end of the Lucite guide through the hole in the rubber membrane and then into the entrance tube of the filter holder; holding the guide and the membrane firmly against the filter holder, roll the rubber "O" ring over the guide and into position around the membrane and in the groove on the entrance tube. It may sometimes be necessary to center the aperture and adjust its diameter by manipulating the rubber membrane. Trim the excess rubber membrane with scissors. Fit a Cambridge filter pad into the

filter holder with the rough side toward the port through which the cigarette is inserted. Position the Teflon gasket with the flat side resting against the filter disc, and screw in the Lucite plug securely against the gasket. Tighten with a special wire wrench with the ends fitted into two sockets on the back of the plug.

Wipe gently with a soft cloth or tissue and weigh the filter assembly to the nearest 0.2 mg. Connect the filter assembly to the smoking machine by a short piece of rubber or other suitable tubing with heavy enough wall so that the cigarette and filter assembly will be held in a horizontal position. Test the smoking apparatus and filter assembly for leaks. Insert a cigarette through the hole in the rubber membrane until the end of the butt is approximately flush with the inner end of the holder tube, i.e., to a depth of about $7/16$ ". Take care that the butt end does not come in contact with the filter disc. Withdraw the cigarette slightly so that the lip of the orifice in the rubber membrane projects outward and forms a snug-fitting collar without crimping or pinching the cigarette. Occasionally, it may be necessary to shift the position of the cigarette slightly in or out, to insure that the collar surrounds the smooth portion of the cigarette and provides a leak-free seal.

There are differences of opinion on the amount or length of each cigarette to be smoked. Results in any event should be expressed so that they are most meaningful.

If all cigarettes are to be smoked to a constant butt length it is recommended that this butt length be 30 mm (the length used by Ogg) or that it be 3 mm beyond the tipping paper (filter overwrap), whichever is the longer, and cigarettes selected for smoking should be marked at this point. If a fixed length of cigarette is to be smoked, e.g., 47 mm, the cigarettes selected for smoking as above described should be marked at this point before insertion into the holder.

Light the cigarette at the beginning of the first puff (an electric coil lighter is suggested). Smoke each cigarette until the burning coal reaches the mark and record the number of puffs taken on each cigarette.

If the operator anticipates that the coal will reach the mark during a puff, he should use judgment whether to allow cigarettes to burn beyond the mark or to stop smoking it short of the mark. In the smoking of cigarettes, "overs" should be balanced with "unders" for each pad. After the last puff, let the cigarette remain in the holder, free-burning, until a few seconds before the next puff will be drawn by the

machine; then quickly remove the butt from the holder and allow a clearing puff of air to draw in the smoke remaining in the entrance port of the assembly. A total of 5 cigarettes is smoked through each filter pad as described. Immediately after 5 cigarettes have been smoked, disconnect the filter assembly from the apparatus, wipe, and weigh to the nearest 0.2 mg.

Record gain in weight of the filter assembly and save smoke samples for water and nicotine analysis.

In smoking care should be taken to smoke a different brand on each port of each machine, and in replicate smokings random selection should be made of ports for brands since some variability between ports may be expected even on the same smoking machine.

The weight of total particulate matter equals the gain in weight of the filter assembly. This weight representing the total particulate matter (wet) from five cigarettes is recorded in mgs.

A total of 40 smokings of 5 cigarettes each is to be made on each brand and the average yield per pad determined.

Determination of Water and Calculation of Dry Particulate Matter

Water may be determined on each pad using the procedure described by Schultz and Spears [Tob. Science 10 (75-76) 1966]. The extract remaining from the water determination is saved for nicotine analysis as described below.

If it is desired, water may be determined separately, i.e., on duplicate smokings using the Karl Fisher procedure essentially as described by Cogbill et al [Tobacco Science 3 (136-138) 1959].

The average yield of water per filter pad is then subtracted from the average yield of total particulate matter (wet) to obtain the average TPM (dry) per pad. This value is used in calculating results as milligrams of dry particulate matter per puff by dividing by the average number of puffs per pad or as mgs. of dry particulate matter per cigarette by dividing the average yield per pad by 5.

Alkaloids (as nicotine)

The apparatus and basic procedures described by Ogg are considered to be satisfactory. If water in TPM is to be determined by the Schultz and Spears procedure, *Take all the sample* an aliquot from the resulting solution is used instead of distilling the alkaloids from the total pad as in the Ogg procedures. The size of aliquot required will depend in part on the alkaloid content of a particular sample and if this value is low, a determination using the Griffith still is preferred since the total distillate volume is one-half that of the modified Kjeldahl still and the concentration is therefore twice as large.

In order to keep the distilland volume as low as possible in the Griffith still procedure it is

considered desirable to acidify the aliquot portion with a smaller volume of more concentrated acid. One ml of 1 N HCl is satisfactory. When working with extracts it is desirable to add the acidified extracts to the Griffith still through a 50 ml separatory funnel.

Reporting of Results

Cigarette smokers vary greatly in their manner of smoking -- puffing rate, volume, frequency, length of cigarette smoked, etc. (The smoke test conditions proposed herein are somewhat arbitrary choices approximating the average smoker.) Certainly not all smokers puff down to a fixed butt length. Consequently for many smokers there may be more meaningful expressions of smoke quantity than that of total quantity delivered per cigarette.

One such approach would be to use a measure of average smoke concentration, that is, the particulate matter or nicotine per unit volume. In the above procedure a convenient unit volume measurement is the standard "puff" so that the smoke concentration would be expressed as "milligrams per puff". This number would be derived by dividing the total delivery of the cigarette smoked by the number of puffs. Such a number, for example, would be more meaningful to a person who only smokes half a cigarette. It is, therefore, recommended that particulate matter and nicotine values be reported both on a "per cigarette" and on a "per puff" basis.

Finally, in reporting results only significant digits should be shown. The sampling and methodological errors in the above procedures only justify results rounded off to the extent indicated below:

	Round off To the Nearest	
	<u>Per Cigarette</u>	<u>Per Puff</u>
Total Particulate Matter (dry)	1 mg.	0.1 mg.
Nicotine	0.1 mg.	0.01 mg.

In other words, on a per cigarette basis the total particulate matter should be expressed only to the nearest milligram.

The use of more precise figures in reporting results implies a precision not justified by either the sampling or by the method described above.